Supercritical Hydrothermal Synthesis of Cr-Substituted CeO2 Nano-Catalysts and the Evaluation of their Catalytic Properties

氏　　名	しゅ　えん　せい 朱　遠　征
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）化学工学専攻
学位論文題目	Supercritical Hydrothermal Synthesis of Cr-Substituted CeO_2 Nano-Catalysts and the Evaluation of their Catalytic Properties （超臨界水熱合成法によるクロム置換セリアナノ触媒の合成と触媒活性の評価）
論文審査委員	主査　東北大学教授　阿尻　雅文　東北大学教授　垣花　眞人 東北大学教授　村松　淳司　東北大学准教授　高見　誠一

論文内容要約

Chapter 1: Introduction

As the world's conventional oil and gas consumption has become increased, new types of natural resources are of keen interest. The Canadian oil sands, bitumen are an important unconventional petroleum resource. The distribution of bitumen in the Athabasca region of Alberta (80% of the total oil sands reserves in Canada) is abundant [1]. Bitumen is a very heavy, carbon-rich and hydrogen lean oils. To produce light oil from the bitumen, upgrading of the bitumen is necessary. The conventional processes for upgrading bitumen including thermal cracking and hydrocracking have a significant problem of large amount of coke formation, which prevents bitumen conversion (less recovery of light oils). Adding hydrogen can be one of the solutions to suppress the coke formation, but this is the large energy consuming process [2]. Hydrothermal cracking is a novel heavy oil upgrading process and can be applied to the bitumen upgrading process [3]. Moreover, metal oxide nano-catalysts having high oxidation capability such as cubic cerium oxide (ceria, CeO_2) nanoparticles are good candidates for the hydrothermal cracking of bitumen, which is called as a catalytic cracking [4]. In this study, high Cr ion substituted CeO_2 nano-catalysts having high oxidative potential were prepared using near/supercritical hydrothermal synthesis and their catalytic properties were evaluated from the relations between the amount of Cr ions in the lattice, oxygen storage capacity and the bitumen conversion.

Chapter 2: Research Background

Supercritical hydrothermal synthesis offers a simple reaction route for metal oxides, which is inherently scalable and environmentally benign. When water is heated up to its critical point (T_c = 374 ºC, P_c = 22.1 MPa), it changes from a polar liquid to a fluid with low dielectric constants and high ionic products (K_w). Under this condition, organic molecules can form homogeneous phase with water and provide organic modification on the metal oxides. The organic modification leads to the control of the exposed surface of the metal oxides. In this manner, {100} facets exposed ceria (cubic CeO_2) was synthesized and showed higher oxygen storage capacity (OSC) than the irregular type of CeO_2 [5].

The catalytic activity of the CeO_2 comes from its OSC property. The oxidative state of Ce can be converted between 3^+ and 4^+ so that the number of oxygen atoms can be changed. The doping (or substitution) of metal ions leads to increate of an oxygen vacancy formation, which increases the oxygen mobility and storage capacity. A large number of studies have shown that rare earth, alkaline earth and transition metals such as Zr^{4+}, Mn^{2+}, Co^{2+}, Cu^{2+} and Ti^{4+} can enhance the OSC property of CeO_2 [6]. Especially, when M^{3+} enters into

CeO_2 lattice, the structure of ceria will follow the charge compensation mechanism so that more oxygen vacancies (oxygen defects) can be formed. The binding energy between the defects strongly follows a function of the substitution ion radius. The smaller ionic radius will lead to the larger defect binding energy, which means that the oxygen defect can stably exist. According to this principle, when the radius of the smaller Cr^{3+} (0.069 nm) replacing Ce^{4+} (0.097 nm), there should be a rich oxygen vacancy formation, thereby enhancing the catalytic potential of CeO_2 nano-catalysts. Based on these background researches, the target of this PHD thesis is confirmed.

Chapter 3: Supercritical Hydrothermal Synthesis of Cr-Substituted Cubic CeO_2 Nanoparticles

The Cr substitution was performed on cubic CeO_2 having higher oxygen storage capacity (OSC). The batch reactor (5 ml) was used for the supercritical hydrothermal synthesis of Cr-substituted CeO_2. Lattice constant of Cr-substituted CeO_2 calculated from XRD patterns decreased compared with cubic CeO_2 owing to substitution of Ce^{4+} (0.097 nm) by the smaller Cr^{3+} (0.069 nm). The morphology of the synthesized nanoparticles was measured using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The particle size was 5–8 nm and the lattice spacing was 0.27 nm that is identical to the exposed {100} facets. The OSC property of Cr-substituted cubic CeO_2 was about two times higher than cubic CeO_2, which implies Ce^{4+} was successfully replaced with Ce^{3+}. However, the substituted amount of Cr was much lower than the loading amount of Cr. This is because Cr^{3+} ions were converted to the by-product before diffusing into the lattice of CeO_2. In order to increase the Cr amount, a rapid heating and mixing system are necessary for the high Cr-substituted CeO_2 nanoparticles.

Chapter 4: Synthesis of Cr-Substituted CeO_2 Using a Rapid Heating Flow-Type Reactor System

In order to realize rapid heating with rapid mixing of the aqueous metal salt with high temperature water, a flow type reactor system was used for the synthesis. Using this system high Cr-substituted CeO_2 NPs were synthesized. The linear relationship between loaded Cr mol% and lattice constants of the particle was obtained. Vegard's law is an empirical rule that illustrates a linear relationship between the lattice constant of substitutional compound and the concentration of the substitution ions. Kim's formula can be applied for the calculation of trivalent substitution ion of CeO_2 using Vegard's slope [7]. The calculated maximum Cr mol% was 38 mol%. The UV-vis spectra of CeO_2 and Cr-substituted CeO_2 nanoparticles were also measured. The substitution of Cr^{3+} ions in the CeO_2 nanoparticles leads to the decrease of Ce^{4+} fraction on the surface, which owing to the replacement of Ce^{4+} by trivalent Cr^{3+} ions. Hence, the red-shift occurs in the absorption spectrum of Cr-substituted CeO_2. The band gap of Cr-substituted CeO_2 decreased with Cr mol% increasing. From these results, concentration of Cr ions in CeO_2 was qualitatively and quantitatively evaluated. Moreover, the OSC of the samples indicated that high Cr-substituted CeO_2 particles have high OSC property.

Chapter 5: Application of Cr-Substituted CeO_2 Nanoparticles: Bitumen Conversion

In this chapter, hydrothermal cracking of bitumen was carried out using Cr-substituted CeO_2 nano-catalysts at 300 and 350 ^oC for 1 h. Asphaltene (heavy fraction of bitumen) conversion gradually increased with increasing Cr substitution amount. Since the more oxygen can release from the higher Cr-substituted CeO_2

nano-catalysts, asphaltene cracking was facilitated with increasing amount of Cr substitution. Moreover, water can oxidize the partially reduced CeO_2 with forming hydrogen (water reforming). As a result, the hydrogen formation is increased with increasing amount of Cr substitution. When hydrothermal cracking reaction was carried out at 300 ºC, hydrogen gas was enhanced as Cr substitution amount increased. However, there was no alkene detected. This might be because C=C bond is difficult to be cracked at relatively low temperature. When hydrothermal cracking was carried out at 350 ºC, the amount of light gases was increased. It reveals that cracking of light fractions and water reforming were promoted. In addition, H_2 could be transferred to alkenes and form alkanes (hydrogenation). The highest asphaltene conversion was 49.8% at 350 ºC with 38 mol% Cr-substituted CeO_2 nano-catalysts.

Chapter 6: Conclusion

In this thesis, high Cr-substituted CeO_2 nano-catalysts were synthesized by using supercritical hydrothermal method. It was found that flow type reactor with rapid heating and mixing is a very effective system for high Cr substitution. Up to 38 mol% Cr was successfully synthesized. The linear relationship between Cr mol% and the lattice constants of the particles was observed that proved the high Cr concentration in CeO_2. In addition, the Cr-substituted CeO_2 showed extremely high oxygen storage capacity. Hydrothermal bitumen cracking was performed with the high Cr substituted CeO_2 nano-catalysts at 300 and 350 ˚C. High asphaltene conversion was obtained with high Cr-substituted CeO_2 nano-catalysts without coke formation. The linear relationship between asphaltene conversion and Cr mol% was also confirmed in both temperature regions.

Reference

[1] Shah A. *et al*., *Energy Environ. Sci.*, **3** (2010), 700–714.
[2] Zhang S. *et al*., *Energy & Fuels,* **21 (**2009), 3057–3062.
[3] Yang M. *et al*., *Catal. Today*, **43 (**1998), 273–280.
[4] Dejhosseini M. *et al*., *Energy Fuels*, **27 (**2013), 4624–4631.
[5] Zhang J. *et al*., *Nano Lett.*, **11 (**2011), 361–364.
[6] Myung J. *et al*., *Int. J. of Hydrogen Energy*, **40 (**2015), 12003–12008.
[7] Kim DJ. *et al*., *J. AM. Ceram. Soc*., **72** (8) (1989), 1415–1421.